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**TEMPERATURE DEPENDENCY OF THE PHOTOABSORPTION  
CROSS SECTION FOR  $\text{CF}_2\text{Cl}_2$**

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TEMPERATURE DEPENDENCY OF THE PHOTOABSORPTION CROSS SECTION  
FOR  $\text{CF}_2\text{Cl}_2$

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The photoabsorption cross section for  $\text{CF}_2\text{Cl}_2$  is measured at 297 K and 200 K. Cross sections are obtained for the ground and first two vibrationally excited states, allowing for a determination of the photoabsorption as a function of temperature over the range of stratospheric interest.

1. Introduction

The photoabsorption cross sections for the chlorofluoromethanes in the ultraviolet have become important recently in connection with potential destructive effects on the stratospheric ozone layer [1,2]. Currently, these cross sections are well known at room temperature [2-4]; however, no information exists at the lower temperatures near 200 K, that exist in the stratosphere where the reactions are of importance. Photoabsorption for transitions from a bound to an unbound state, as is the case for the chlorofluoromethanes, is basically described by the Frank Condon principle. The cross sections display a maximum value at some wavelength and decrease progressively as the wavelength recedes from this maximum. The width of this

curve is governed basically by the vibrational amplitude of the molecule. A decrease in temperature populates lower vibrational levels with resulting smaller amplitudes; consequently, a more rapid decrease in the shoulders of the cross-section curve is expected. For the wavelength range of interest for the stratospheric photoabsorption of chlorofluoromethanes, the cross sections are on the rapidly decreasing shoulder of such a curve. Hence, a reduction in temperature is expected to cause a corresponding reduction in the desired cross section.

Measurements are presented here showing the effect of reducing the temperature on photoabsorption by  $\text{CF}_2\text{Cl}_2$  (dichlorodifluoromethane). Cross sections are obtained over the wavelength range of stratospheric interest at both 297 K and 200 K. From these measurements, cross sections for the ground and first two vibrational states are determined allowing for a computation of the total cross section as a function of temperature.

## 2. Experiment

Photoabsorption cross sections for  $\text{CF}_2\text{Cl}_2$  were obtained at 25-Å intervals from 1700 Å to 2100 Å at room temperature ( $297 \pm 1$  K) and at  $200 \pm 2$  K. The lower temperature was obtained by refrigerating the test chamber with a mixture of dry ice and isopropyl alcohol. Radiation at the desired wavelength was provided by passing the continuum ultraviolet radiation from a deuterium microwave discharge through a McPherson 0.3-m vacuum monochromator. The resulting radiation traversed an absorption cell of 10.35 cm in length was detected with an EMI G26H315 ultraviolet photomultiplier. All intermediate optical elements were made from calcium fluoride, and the entire optical path could be evacuated. Pressure in the absorption cell was measured with a Datametrics barocel electronic manometer utilizing a 0-100 torr transducer

calibrated to an accuracy of 0.5%. Pressures utilized throughout the experiment were between 0.22 and 100 torr at 297 K but were limited to below 60 torr at 200 K to avoid condensation within the refrigerated chamber.

Cross sections for each wavelength were obtained, assuming Lambert Biers law to be valid, on observing transmission through the cell as a function of gas pressure. Approximately five transmission pressure readings were used to obtain a single cross section. Additionally, five such measured cross sections were obtained for each wavelength on different days of operation to provide the final statistically averaged data. The total systematic error introduced from inaccuracies of electronics, pressure measurements, and monochromator adjustments did not exceed 1%. Statistical uncertainties with transmission readings gave rms uncertainties in the obtained cross sections typically of 1-2% but increased to nearly 10% at the lowest measured cross section. Therefore, the total uncertainty of the data was typically 3% and did not exceed 10%.

### 3. Results

Results for the measured photoabsorption cross sections at 297 K and 200 K are shown in table 1. At room temperature the data are found to be in excellent agreement with the measurements of Rowland and Molina [2] and with Robbins et al. [4]. The difference is typically much less than the combined uncertainty of the sets of data. At the lower temperature, a marked decrease in the cross section as compared to the room temperature data is observed above 1800 Å. Such a decrease is accounted for by a decrease in the vibrational excitation of the molecule.

For stratospheric considerations, it is desirable to determine the spectral photodissociation cross section as a function of temperature. Since the quantum yield of generating chlorine atoms from  $\text{CF}_2\text{Cl}_2$  with photon absorption is unity [5], the cross section for photoabsorption is equal that for photodissociation. The total cross section  $\sigma$  at a given wavelength can be determined from the sum of the cross sections  $\sigma_i$  for each vibrational state  $i$  times the relative population  $N_i/N$  of that state:

$$\sigma = \sum_i \frac{N_i}{N} \sigma_i, \quad \text{where } N = \sum_i N_i. \quad (1)$$

As a function of temperature, the individual state cross sections essentially remain constant but the population of each individual state varies considerably. For  $\text{CF}_2\text{Cl}_2$  there are nine vibrational modes to contribute to the excitation of the molecule. Over the temperature range of interest, however, only bending of the C-Cl bond is appreciably excited to affect the results. This excitation can be characterized by a fundamental frequency of  $261 \text{ cm}^{-1}$  [6].

A consideration of different fundamental frequencies, though affecting the calculations on population distributions of the states, has a minimal effect on the resultant temperature-dependent total cross section. For  $\text{CF}_2\text{Cl}_2$  over the temperature range of interest for atmospheric considerations, only the ground state, the first vibrational state, and to a lesser extent the second vibrational state are appreciably populated to contribute to the total cross section. The relative population of these states is shown in table 2 for 200 K and 297 K.

The contributions of the third and higher vibrational states are minor but lumped into the second state here for completeness. In the intermediate temperature range, the individual state populations are essentially linear such that their values can be accurately predicted by the relationships:



$$N_0/N = 1.113 - 1.327 \times 10^{-3} T, \quad (2)$$

$$N_1/N = -0.02174 + 7.567 \times 10^{-4} T, \quad (3)$$

$$N_2/N = -0.08973 + 5.651 \times 10^{-4} T, \quad \text{with } T \text{ in } ^\circ\text{K}. \quad (4)$$

Knowing the population of the three significant states at the two temperatures at which the total cross sections were measured, the cross sections for each state can be determined. It is expected from the Frank Condon principle that individual states with higher vibrational excitation will exhibit a broader wavelength dependency to the cross section than the lower states. The maximum value itself will probably decrease slightly with increasing excitation. Since the population of the second vibrational state is relatively small and if its cross section does not differ drastically from that of the first state, the cross sections for the ground and first vibrational states can be obtained from the experimental data with a reasonable accuracy. This is the case for the  $\text{CF}_2\text{Cl}_2$  data for wavelengths between 1700 Å and 2000 Å. Above this wavelength, the ground-state cross section, as calculated from the data, becomes small enough that the first and second vibrational states dominate the total cross section. Therefore, the cross sections for these two states can be determined in this range. Least squares fits of these individual-state data were obtained in semilog form in a polynomial expansion. A parabolic form was quite representative for each state though a cubic relationship slightly improved the ground-state relationship. Higher order terms did not significantly improve the overall accuracy. These individual-state cross sections can be represented by:

$$\log_{10} \sigma_0 = 344.9399 - 0.661837 \lambda + 4.00541 \times 10^{-4} \lambda^2 - 8.04456 \times 10^{-8} \lambda^3 \quad (5)$$

for  $\lambda < 2025$ ,  $\sigma_0 = 0$  for  $\lambda > 2025$ ,

$$\log_{10} \sigma_1 = -89.41827 + 0.0792792 \lambda - 2.19343 \times 10^{-5} \lambda^2, \quad (6)$$

$$\log_{10} \sigma_2 = -73.8016 + 0.062135 \lambda - 1.72398 \times 10^{-5} \lambda^2, \quad (7)$$

with dimensions for  $\sigma$  in square centimeters and  $\lambda$  in angstroms. These results are shown in fig. 1. The rms deviation of these computed values compared to the calculated values is 4.8% for the ground state, 5.6% for the first vibrational state, and 4.8% for the second vibrational state.

The cross sections for photodissociation of  $\text{CF}_2\text{Cl}_2$  as a function of temperature and wavelength can be calculated utilizing expressions (1) through (7). A comparison of the original experimental data with the corresponding calculated values indicates good agreement. At 297 K the rms deviation is 5.9% with an average error of 2.2%. At 200 K the rms deviation is 8.5%, and the average error is 1.2%. The maximum occurs at the lowest cross sections where the error of the original data is largest. However, the contribution to the photodissociation rate at these wavelengths has diminished significantly such that the contribution to the total is negligible. It is expected that the total uncertainty in determining the photodissociation cross section for  $\text{CF}_2\text{Cl}_2$  over the temperature range of atmospheric interest as given here is less than 5%.

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Table 1

Photoabsorption cross sections for  $\text{CF}_2\text{Cl}_2$ 

| $\lambda$ (Å) | $\sigma$ 297 K (cm <sup>2</sup> ) | $\sigma$ 200 K (cm <sup>2</sup> ) |
|---------------|-----------------------------------|-----------------------------------|
| 1700          | $1.20 \times 10^{-18}$            | $1.24 \times 10^{-18}$            |
| 1725          | $1.53 \times 10^{-18}$            | $1.60 \times 10^{-18}$            |
| 1750          | $1.75 \times 10^{-18}$            | $1.82 \times 10^{-18}$            |
| 1775          | $1.82 \times 10^{-18}$            | $1.91 \times 10^{-18}$            |
| 1800          | $1.73 \times 10^{-18}$            | $1.77 \times 10^{-18}$            |
| 1825          | $1.47 \times 10^{-18}$            | $1.45 \times 10^{-18}$            |
| 1850          | $1.12 \times 10^{-18}$            | $1.07 \times 10^{-18}$            |
| 1875          | $8.47 \times 10^{-19}$            | $7.62 \times 10^{-19}$            |
| 1900          | $6.15 \times 10^{-19}$            | $5.13 \times 10^{-19}$            |
| 1925          | $4.01 \times 10^{-19}$            | $3.24 \times 10^{-19}$            |
| 1950          | $2.33 \times 10^{-19}$            | $1.69 \times 10^{-19}$            |
| 1975          | $1.48 \times 10^{-19}$            | $9.93 \times 10^{-20}$            |
| 2000          | $8.27 \times 10^{-20}$            | $5.00 \times 10^{-20}$            |
| 2025          | $4.39 \times 10^{-20}$            | $2.49 \times 10^{-20}$            |
| 2050          | $2.51 \times 10^{-20}$            | $1.30 \times 10^{-20}$            |
| 2075          | $1.44 \times 10^{-20}$            | $6.61 \times 10^{-21}$            |
| 2100          | $7.61 \times 10^{-21}$            | $3.35 \times 10^{-21}$            |
| 2125          | $3.87 \times 10^{-21}$            | $1.86 \times 10^{-21}$            |
| 2150          | $2.18 \times 10^{-21}$            |                                   |

Table 2

Vibrational state population distribution

| Population | 200 K  | 297 K  |
|------------|--------|--------|
| $N_0/N$    | 0.8474 | 0.7188 |
| $N_1/N$    | 0.1295 | 0.2030 |
| $N_2/N$    | 0.0231 | 0.0781 |

Figure Caption

Fig. 1. Photoabsorption cross section vibrational states of  $\text{CF}_2\text{Cl}_2$ .

PHOTOABSORPTION CROSS SECTION,  
VIBRATIONAL STATES  $\text{CF}_2\text{Cl}_2$

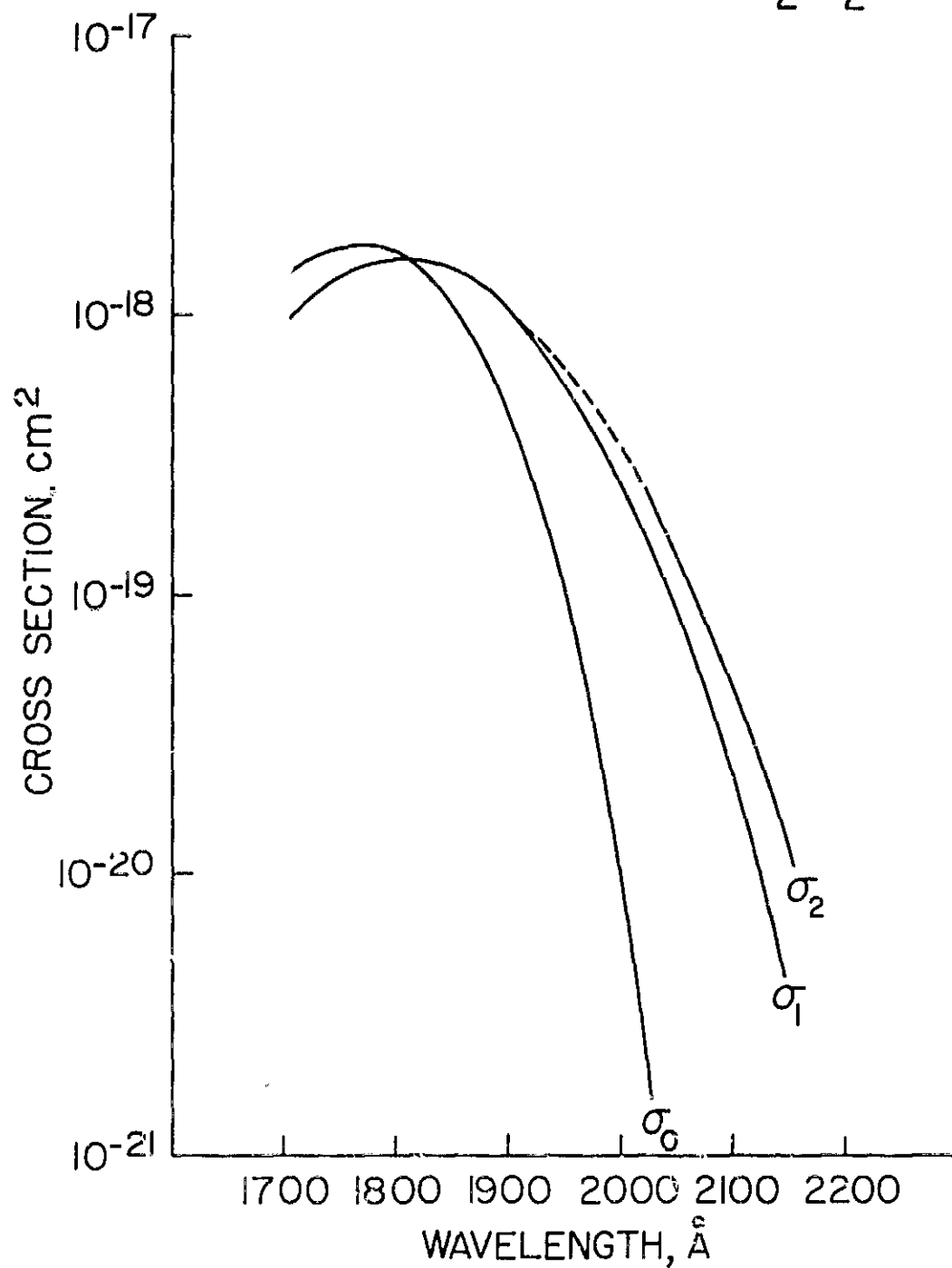


Fig. 1